only. Thus the spin angular momentum **s** is given by:

$$\mathbf{s} = \sqrt{s(s+1)}\frac{h}{2\pi} = \sqrt{\frac{1}{2}\times\frac{3}{2}}\text{ units},$$
$$= \tfrac{1}{2}\sqrt{3}\text{ units}. \qquad (5.10)$$

The quantization law for spin momentum is that the vector can point so as to have components in the reference direction which are *half-integral* multiples of $h/2\pi$, i.e. so that $\mathbf{s}_z = s_z h/2\pi$ with s_z taking the values $+\frac{1}{2}$ or $-\frac{1}{2}$ only. The two (i.e. $2s+1$) allowed directions are shown in Fig. 5.4(*c*); they are normally degenerate.

5.5. Total Electronic Angular Momentum. We now need to discover some means whereby the orbital and spin contributions to the electronic angular momentum may be combined. Formally we can write:

$$\mathbf{j} = \mathbf{l}+\mathbf{s}, \qquad (5.11)$$

where **j** is the *total angular momentum*. Since **l** and **s** are vectors, equation (5.11) must be taken to imply *vector addition*. Also formally, we can express **j** in terms of a total angular momentum quantum number j:

$$\mathbf{j} = \sqrt{j(j+1)}\frac{h}{2\pi} = \sqrt{j(j+1)}\text{ units}, \qquad (5.12)$$

where j is *half-integral* (since s is half integral for a one-electron atom), and a quantal law applies equally to **j** as to **l** and **s**: **j** *can have z-components which are half-integral only*, i.e.

$$j_z = \pm j, \pm(j-1), \pm(j-2), \ldots, \tfrac{1}{2}. \qquad (5.13)$$

There are two methods by which we can deduce the various allowed values of **j** for particular **l** and **s** values. We shall consider them both briefly.

(*i*) Vector Summation. In ordinary mechanics two forces in different directions may be added by a graphical method in which vector arrows are drawn to represent the magnitude and direction of the forces, the "parallelogram is completed" and the magnitude and direction of the resultant given by the diagonal of the parallelogram. Exactly the same method can be used to find the resultant (**j**) of the vectors **l** and **s**. The important difference is that quantum mechanical laws restrict the angle between **l** and **s** to values such

that $\mathbf{j}$ is given by equation (5.12) with *half-integral* j. Thus $\mathbf{j}$ can take values

$\frac{1}{2}\sqrt{3}, \frac{1}{2}\sqrt{15}, \frac{1}{2}\sqrt{35}, \ldots$ corresponding to $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$.

The method is illustrated in Fig. 5.5(*a*) and (*b*) for the case $l=1$ (i.e. $\mathbf{l}=\sqrt{2}$) and $s=\frac{1}{2}$ ($\mathbf{s}=\frac{1}{2}\sqrt{3}$). In (*a*) the summation yields $\mathbf{j}=\frac{1}{2}\sqrt{15}$, which corresponds to a j-value of $\frac{3}{2}$, while in (*b*) $\mathbf{j}=\frac{1}{2}\sqrt{3}$ or $j=\frac{1}{2}$. Construction or calculation shows that $\mathbf{l}$ and $\mathbf{s}$ may not be combined in any other way to give an allowed value of $\mathbf{j}$.

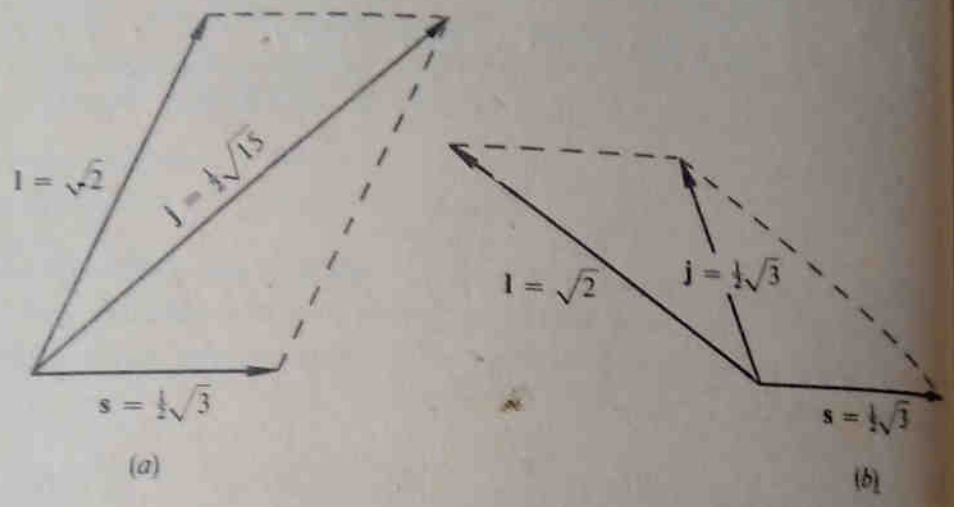

Fig. 5.5: The two energy states having different total angular momentum which can arise as a result of the vector addition of $\mathbf{l}=\sqrt{2}$ *and* $\mathbf{s}=\frac{1}{2}\sqrt{3}$.

Note that we can get exactly the same answer by summing the *quantum numbers* l and s to get the *quantum number* j. In this example $l=1$, $s=\frac{1}{2}$, and hence:

$$j = l+s = \tfrac{3}{2}, \quad \text{or} \quad j = l-s = \tfrac{1}{2}.$$

This simple approach, although adequate for systems with one electron only, is not readily extended to multi-electron systems. For these we must use the rather more fundamental method outlined below.

(*ii*) Summation of z-Components. If the components along a common direction of two vectors are added, the summation yields the component in that direction of their resultant. We have seen (cf. equation (5.9)) that the z-components of $l=1$ are ± 1 and

while those of $s=\frac{1}{2}$ are $\pm\frac{1}{2}$ only. Taking all possible sums of these quantities we have:

$$j_z = l_z + s_z$$
$$\therefore j_z = 1+\tfrac{1}{2},\ 1-\tfrac{1}{2},\ 0+\tfrac{1}{2},\ 0-\tfrac{1}{2},\ -1+\tfrac{1}{2},\ -1-\tfrac{1}{2};$$
$$= \tfrac{3}{2},\ \tfrac{1}{2},\ \tfrac{1}{2},\ -\tfrac{1}{2},\ -\tfrac{1}{2},\ -\tfrac{3}{2}.$$

In this list of six j_z components, the maximum value is $\frac{3}{2}$, which we know (cf. equation (5.13)) must belong to $j=\frac{3}{2}$. Other components of $j=\frac{3}{2}$ are $\frac{1}{2}$, $-\frac{1}{2}$ and $-\frac{3}{2}$ and, striking these from the above six, we are left with $j_z=+\frac{1}{2}$ and $-\frac{1}{2}$. These values are plainly consistent with $j=\frac{1}{2}$.

Thus all the six components are accounted for if we say that the states $j=\frac{3}{2}$ and $j=\frac{1}{2}$ may be formed from $l=1$ and $s=\frac{1}{2}$. This is, of course, in agreement with the vector summation method.

Both these methods show that for a p electron (i.e. $l=1$), the orbital and spin momenta may be combined to produce a total momentum of $\mathbf{j}=\frac{1}{2}\sqrt{15}$ when $\mathbf{l}$ and $\mathbf{s}$ reinforce (physically we would say that the angular momenta have the same *direction*) or to give $j=\frac{1}{2}\sqrt{3}$ when $\mathbf{l}$ and $\mathbf{s}$ oppose each other. Thus the total momentum is different in *magnitude* in the two cases and hence we have arrived at two *different energy states* depending on whether $\mathbf{l}$ and $\mathbf{s}$ reinforce or oppose. Both energy states are p states, however (since l is 1 for both), and they may be distinguished by writing the j quantum number value as a subscript to the *state symbol* P, thus $P_{3/2}$ or $P_{1/2}$. (We here use a capital letter for the state of a whole atom and a small letter for the state of an individual electron; in the hydrogen atom, which contains only one electron, the distinction is trivial.) States such as these, split into two energies, are termed *doublet states*; their doublet nature is usually indicated by writing a superscript 2 to the state symbol, thus: ${}^2P_{3/2}$, ${}^2P_{1/2}$. The state (or term) symbols produced are to be read "doublet p three halves" or "doublet p one half" respectively.

All other higher l values for the electron will obviously produce doublet states when combined with $s=\frac{1}{2}$; for instance, $l=2, 3, 4, \ldots$ will yield ${}^2D_{5/2,\,3/2}$, ${}^2F_{7/2,\,5/2}$, ${}^2G_{9/2,\,7/2}$, etc. The student should satisfy himself of this, preferably by using the z-component summation method outlined above. There is, however, a slight difficulty with s states ($l=0$). Here, since $j=0$, it can make no contribution